BAGDASAR'YAN, Kh. S.

"Photochemical Polymerization of Vinyl Compounds," Thesis for degree of Dr. Chem. Sci. Sub. 26 Jun 50, Sci. Res. Order of Lenin Red Banner Physical Chemistry Inst. im. Karpov, Moscow

Sum. 71, 4 Sep 52

CA Chabhankynd, KH.S.

Bond energies and departure from the additivity rule in hydrocarbons. Kh. S., Bagdasar'yan (Karpov Phys.-Chem. Inst., Moscow). Zhur. Fiz. Khim. 24, 1329-38 (1950).—A new set of bond energies is proposed, based on the value of 170 keal. for the sublimation heat of diamond: H—H 104; C—C 81; C—C 145-5; C—C 195; C—H 97-5; C—H 97-5 × 2; C 11, 98 × 3; C@H, 99 × 4. This set gives correct values (within 0.2 keal./mole) for the heats of formation of all normal satd. hydrocarbons and of C₃H₄. Pos. (P) and neg. (N) departures from additivity are obtained by comparing calcd. values with heats of combustion (Rossini) and of hydrogenation (Kistlakowsky) for various comples. For butadene, the additive hydrogenation heat is $[(2 \times 84) + (4 \times 97.5) + (2 \times 1.5)] + [(2 \times 104) + (2 \times 145.5)] = 62$. The exptl. value is 57.1 and thus the resonance energy is 4.9, which is in good agreement with 5.2, the value obtained from the combustion heat. For iso satd, comples, tables show that (1) a Megroup in the 2-position does not give noticeable departures from additivity; a shift of the group towards more central positions gives N. Et groups give stronger N. This effect is possibly due to steric hindrance. (2) The presence of two or three Me groups on a 2-C atom gives P(e.g. EtCMe₃) but a N effect is displayed by PrCMe₃Et and similar compds. (3) Two Me groups on 2 neighboring C-atoms give a N effect. This N effect decreases when the Me groups are moved away from each other along the chain. Cyclopentane gives N = 0.5, whereas cyclohexane gives N = 0.6 (stram). Substitution of Me groups at a double bond gives P 1 about 1). This P effect increases with the no of substitutions and is stronger for asym, than for sym substitutions (hyperconjugation and steric effects). All cyclic compds. with 1 double bond give P effects. Mols, with isolated double bonds give rifects which are approx.

the sum of the effects due to each double bond, e.g. for limonene P=6.4 whereas P=2.8 for Me_5C :CH₂ and P=3.2 for Me_5C :CHMe. Mols. with conjugated double bonds present large effects (resonance). The calcel resonance energy of CaH₆ is 38.7 (from combustion) and 38.6 (from hydrogenation). Substitutions of Me_5E : An analysis of CaH₆ with a double bond gives P effects (Conjugation of CaH₆ with a double bond gives P effects (styrene, 4) Data also show that hyperconjugation is more important with triple than with double bonds. Allenes present N effects (approx. 9). Allyl ale, gives N=0.5, which is anomalous. Resonance between vinvl and carbonyl groups is 3.4 kcal. (calcd. for McCH:CHCHO). For E_5O the resonance energy is 4.3 kcal. Resonance energies E of various radicals are calcd with the help of the proposed set of bond energies and the data of Steacie, Roberts, and Sgware. $E=U_R=U_{R\to G}$, and $U_R=U=D$, where U_R is the ealed, value based on the additivity rule; U is the heat of formation of the mod with said valences; D is the dissoon, energy into radicals. A proof of the consistency of the set of bond energies (and in particular of the value 170 for the sublimation heat of diamond) is provided by the good agreement between calcd, and evptl. dissoen, energies; this agreement is obtained without special assumptions.

1951

which the aromatic nuclei are conjugated together, or

of E for hydrocarbons like pyrene and perylene than the method of molecular orbits. For hydrocarbons in

meric hydrocarbons. This method gives lower values

However, the electronic gas method does not reflect

incident with the results of quantum-chem calcs.

differences in the energies of conjugation of iso-

polynuclear aromatic hydrocarbons led to results co-

with a double bond, the electronic gas method gives

APPROVED FOR RELEASE: 06/06/2000

USSR/Chemistry - Aromatic Hydrocarbons

Jul 52

EACDASARIYAN,

"Examination of Aromatic Hydrocarbons by the Electronic Gas Method," Kh. S. Bagdasar'yan, (letter to the Editor), Physicochem Inst imeni L. Ya. Karpov, Moscov

Zhur Fiz Khim, Vol 26, No 7, pp 1053-1056

In aromatic hydrocarbons, the T-electrons are "free"

248II15

analagous to valence electrons in metals. This suggests, the author states, that the ciectronic gas method be applied to an examination of the properties

of aromatic hydrocarbons. Use of this method to calc

Tug4

PA SLBILS

gas method.

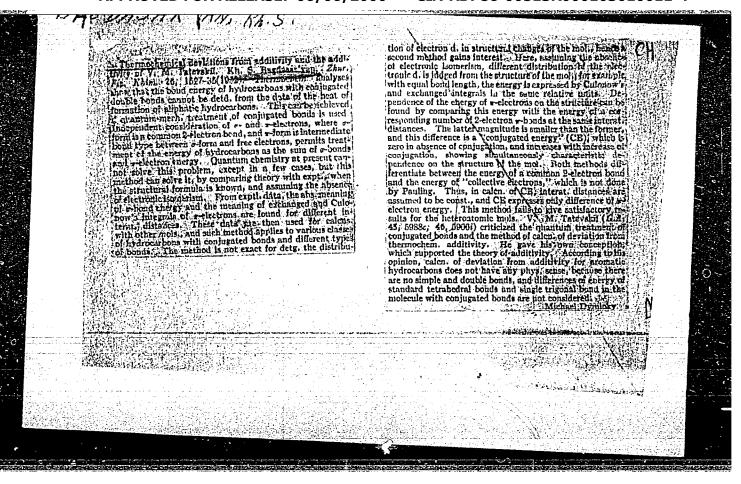
results approximately coincident with the results of the molecular orbits method. Calcn of the potential energy of electronic gas, the author states, will permit more precise computations by the electronic

This, he adds, is being done.

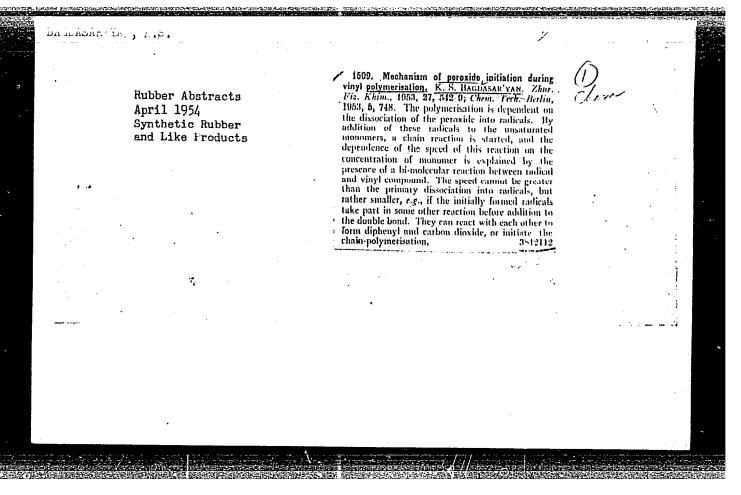
CIA-RDP86-00513R000103010011-4"

KH.

٠\$



-	Decomposition of Settler's percentle in different survents. Kh. S. Bagdasar's an and R. I. Milyutinskava (L. Ya. 1993) 1993 1993 1993 1994 1995 1995 1995 1995 1995 1995 1995	
	O.185 mol./1., it decomposes 7 times as fast in AcOBt, and 4 times as fast in AcOH as in CaH ₂ . In acctone the rate of decompose is twice that in CaH ₃ , and in CCh ₄ , Ph ₂ CH ₂ , dibutyl phthalate, and pseudocumene about the same as in CaH ₃ . With decreasing conen. of B2/O ₂ in CaH ₃ the yield of B2OH decreases. In AcOH such a relation does not hold for either CO ₂ or B2OH. At a conen. of O.185 mole l in Ph ₂ CH ₂ , the yield of B2OH. At a conen. of O.185 mole l in Ph ₂ CH ₃ , the yield of B2OH is twice that in CaH ₄ ; in dibutyl phthalate 1.4 times, in account twice, and in AcOH 5 times. The yield of more than the Ph ₂ CH ₃ is an account twice, and in AcOH 5 times. The yield of the May are the CaH ₃ in CaH ₄ , in the presence of vinyl compds. in CaH ₄ , at 75° results in a decreased yield of B2OH and CO ₂ . There exections are attributed to a chain decompn. of B2O ₂ . There are 2 types of decomposition of decompn.	
	teraction of peroxide with mot, reacting components. Jack Weiner	



BEGDASARYAN, KH.S.. USSR/Chemistry

Card 1/2

Authors

: Bagdasaryan, Kh. S., and Milyutinskaya, R. I.

Title

: Photochemical Reactions of carbon tetrachloride with vinyl compounds

Periodical

: Zhur. Fiz. Khim. 28, Ed. 3, 498-506, March 1954

Abstract

The exposure of carbon tetrachloride mixtures to the effect of vinyl compounds leads to a more or less considerable increase in the rate of polymerization or the formation of carbon tetrachloride addition products with double bond. Typical is the behavior of styrene and vinyl butyl ether. Styrene dissolved in carbon tetrachloride polymerizes much faster than in an inert solvent. The molecular weight of polymers decreases simultaneously, Styrene is a photoactive component; the increase in the rate of polymerization is caused by the increase in the rate of formation of primary radicals. Vinyibutyl ether mixed with carbon tetrachloride forms an addition product with composition ratio of 1:1. The rate of reaction is proportional to the first degree of light intensity, the thermal

Zhur. Fiz. Khim. 28, Ec. 3, 498-506, March 1954

Card 2/2

Abstract

coefficient is close to one. It is a chain reaction. The quantum yield increases during the reduction in the ether concentration and reaches several thousands in diluted solutions. Hexachloroethane chloroform, and allyl chloride also accelerate the photopolymerization of vinyl compounds but to a much lesser degree than carbon tetrachloride. Seven USSR references. Table, graphs.

Institution

t The L. Ya. Karpov Physico-Chemical Institute, Moscow, USSR.

Submitted

: June 19, 1953

BAGDASARYAN, Kh. S.

USSR/Chemistry

Card 1/1

Authors

: Milyutinskaya, R. I., and Bagdasaryan, Kh. S.

Title

: Study of the mechanism of radical reactions. Part 3. - Decomposition of benzoyl peroxide and its p, p'-dinitro- and p, p'-dimethoxy-derivatives in benzene and nitrobenzene.

Periodical

: Zhur. Fiz. Khim., 28, Ed. 5, 797 - 800, May 1954

Abstract

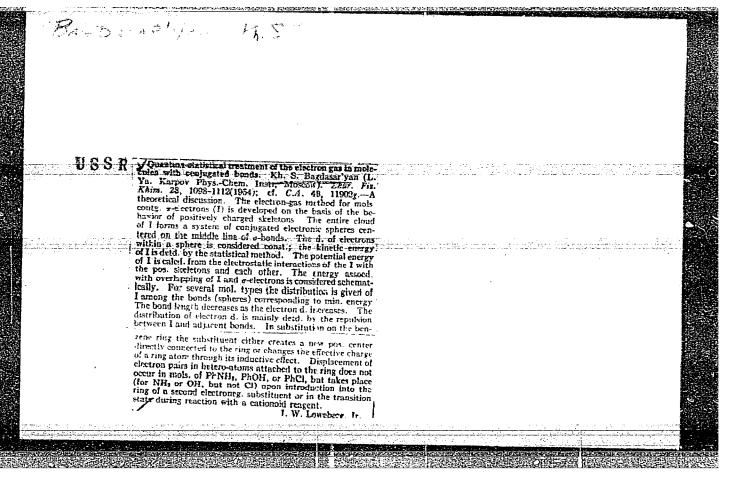
the decomposition of benzoyl peroxide and its dinitro- and dimethoxy-derivatives in benzene and nitrobenzene was used as an example to prove the value of the polarity of molecules and free radicals for the process of radical reactions. The polarity of radicals may at times have a double effect on the rate of radical reactions. At distances up to the sum of the van der Waals radii, the opposite polarity of the reacting components should be favorable for the radical reaction by increasing the number of collisions. Seven references: 6-USSR; 1-USA. Table.

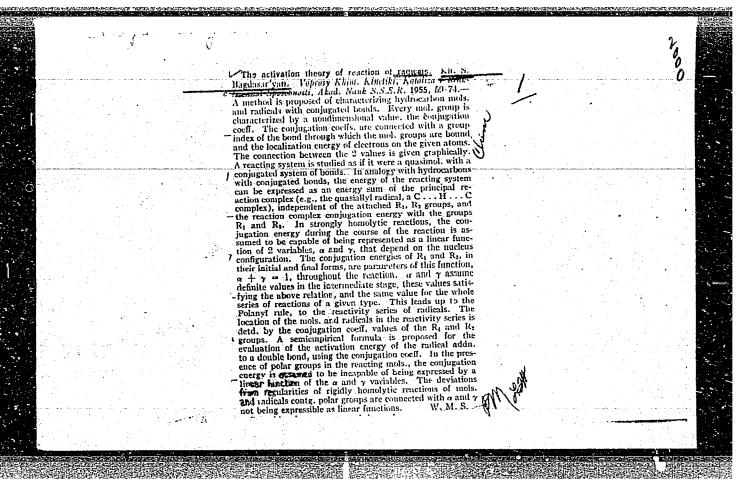
Institution :

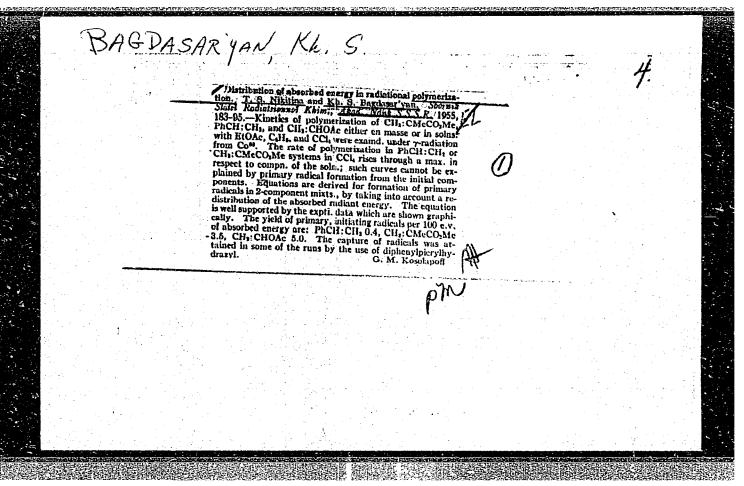
The L. Ya. Karpov Physico-Chemical Institute, Moscow.

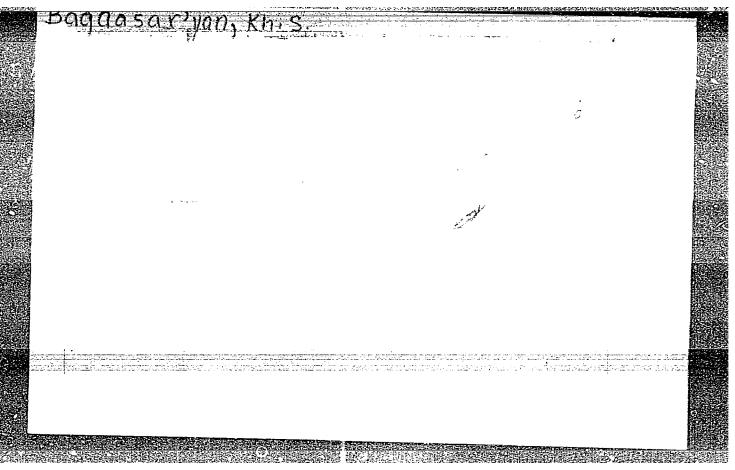
Submitted

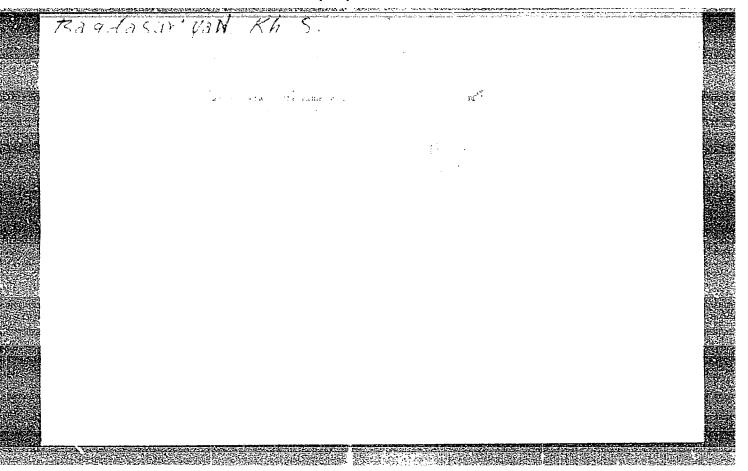
July 3, 1953

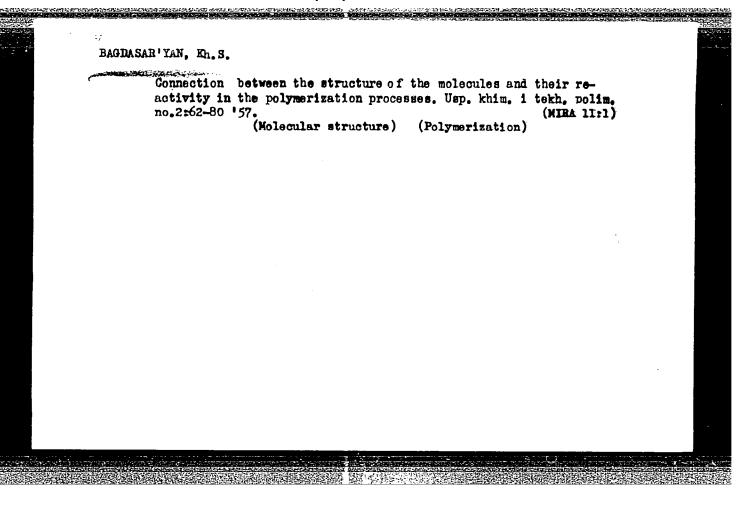












BAGDASAR

USSR/Physical Chemistry - Radiation Chemistry, Photochemistry, Theory of Photographic Process.

B-10

Abs Jour: Referat. Zhurnal Khimiya, No 3, 7268.

Author : T.S. Wikitina, Kh. S. Bagdasar'yan.

Inst

: Addition of Carbon Tetrachloride to Vinylbutyl Ester under Title

J-Radiation Action.

Orig Pub: Zh. fiz. khimii, 1957, 31, No 3, 704-707.

Abstract: A product of addition of carbon tetrachloride to vinylbutyl ester (I) in the proportion of 1:1 is formed by the action of γ -radiation of Co 60 on mixtures of I and CCll. The reaction rate depending on the mixture composition passes through a maximum at 65 mol. % of CCl4; the yield from such a mixture is 4500 per 100 ev of absorbed energy. The yield of radicals from I and from the equimolecular mixture of I and CCl1 is 4.8 and 13 (determined with diphenylpicrylhydrazyl). A chain reaction mechanism is pro-

posed. See also RZhKhim, 1956, 445.

: 1/1 Card

-8-

BHGDASAK YAND AM. O.

MILYUTINSKAYA, R.I.; BAGDASAR'YAN, Kh.S.; IZRAILEVICH, Ye.A.

Studies on the mechanism of radical reactions. Part 4: The mechanism of formation of diphenyls in the decomposition of benzoyl and 4-nitrobenzoyl peroxides in benzene and nitrobenzene [with summary in English]. Zhur. fiz. khim. 31 no.5:1019-1026 My 157. (MIRA 10:11)

1. Fiziko-khimicheskiy institut im. L. Ya. Karpova, Moskva.
(Benzene) (Benzoyl peroxide)

AUTHORS:

Krongauz, V. A., Bagdasar'yan, Kh. S.

20-114-4-41/63

TITLE:

Energy Transfer on the Occasion of the Radiolysis of Benzoyl Peroxide Solutions (Peredacha energii pri radiolize rastvorov

perekisi benzoila)

PERIODICAL:

Doklady Akademii Nauk SSSR, 1957, Vol. 114, Nr 4,

pp. 829-832 (USSR)

ABSTRACT:

Under the influence of ionizing radiation upon organic solutions the primarily absorbed energy may be transferred from one component to another. In order to determine the influence which the quality of the solvent exerts upon the energy transfer, the authors studied the radiolysis of benzoyl peroxide solutions in benzol, cyclohexane and ethylbenzoyl peroxide solutions are corried out by y-rays Co⁶⁰ in the

acetate. The radiolysis was carried out by γ -rays Co^{60} in the absence of air. The initial velocity of the peroxide decomposition was measured iodometrically. Its decomposed

amount did not exceed 10-20% of its initial concentration. Figure 1 shows the dependence of the initial velocity of the radiolysis on the initial concentration. The benzoylperoxide absorbs part of the total energy absorbed by the solution,

absorbs part of the total energy absorbed by the peroxide this part corresponding to the electron share of the peroxide

Card 1/4

Energy Transfer on the Occasion of the Radiolysis of Benzoyl 20-114-4-41/63 Peroxide Solutions

mechanism. One may assume that the high radiation yield in the radiolytic decomposition of the peroxide is due to the energy transfer of primarily produced benzol molecules upon the peroxide molecules. A comparison of the results obtained from radiolyses of benzoylperoxide in different solvents shows that the energy transfer from the solvent upon the solved substance is dependent on the quality of the solvent. The individual stages of the radiolysis are as follows: 1) Formation of excited benzol molecules at the absorption of the radiation energy, 2) a spontaneous disactivation of the same molecules. 3) energy transfer of the excited benzol molecules upon the peroxide and the decomposition of the latter, and 4) decomposition of the peroxide by absorption of the γ -rays by the There are 4 figures and 12 references, 2 of which are Soviet.

ASSOCIATION:

Nauchno-issledovatel'skiy fiziko-khimicheskiy institut im. L. Ya. Karpova (Scientific Research Institute for Physical Chemistry imeni L. Ya. Karpov)

Card 3/4

BAGDASAR'YAN, KH.S

AUTHORS:

Krongauz, V. A., Bagdasar'yan, Kh. S.

20-5-27/48

TITLE:

Radiation Chemical Effect of Excitation Energy Transfer in Three-Component Solutions (Radiatsionnokhimicheskiy effekt perekhoda energii vozbuzhdeniya v trekhkomponentnykh

rastvorakh).

PERIODICAL:

Doklady AN SSSR, 1957, Vol. 116, Nr 5, pp. 817-819 (USSR).

ABSTRACT:

The authors showed already in preliminary works (reference 1-2) that with the radiolysis of solutions of benzene-super-oxide in benzene the primary absorbed energy is transfered from the excited benzene molecules to the molecules of superoxide. In order to closer study the mechanism of energy transfer of the radiolysis of the three-component benzene + phenantrene + benzoyl-superoxide, the present work investigates the kinetics of the radiolytic decomposition of benzoyl-superoxide of these compounds within a wide range of phenantrene concentrations. (0 - 1 mol/1) with three different concentrations of benzoyl-superoxide (0,0125; 0,0083; 0,0042 mol/1). The radiolysis of the solutions was carried out under the influence of \(\gamma - \text{ rays of } \) Co \(\frac{60}{2} \) with

Card 1/3

APPROVED FOR RELEASE: 06/06/2000 CIA-RDP86-00513R000103010011-4"

Radiation Chemical Effect of Excitation Energy Transfer 20-5-27/48 in Three-Component Solutions.

no air present. The differential dose was 1,5.10¹⁵ eV/ml.sec. A diagram shows the dependence of the initial velocity of the radiolysis of benzoyl-superoxide on the concentration of phenantrene for three concentrations of superoxide. With increasing concentration the velocity of radiolysis decreases at first, passes aminimum and then increases linearly. The authors study seven processes occuring with the radiolysis of the compounds investigated. They take the following simplified conditions as basis: As the concentration of benzoyl-superoxide in the solution is small the decomposition of the superoxide by direct influence of radiation can be neglected. The decomposition of the excited molecules of benzene and phenantrene to their radicals is not taken into account because of the small yield of radiation of the radicals of these hydrocarbons. The excited phenantrene molecules obtained by means of two certain (mentioned) reactions are kinetically identical. A formula is given for the velocity of the radiolytic decomposition of benzoyl-superoxide and it is specialized for sufficiently great concentrations of phenantrene. In the end the authors still estimate the mean life of the

Card 2/3

AUTHOR: Bagdasar'yan, Kh.S. SOV-77-3-5-13/21

TITLE: The Mcchanism of the Action of Dye-desensitizers (K mekha-

nizmu deystviya krasiteley-desensibilizatorov)

PERIODICAL: Zhurnal nauchnoy i prikladnoy fotografii i kinematografii,

1958, Vol 3, Nr 5, pp 381-382 (USSR)

ABSTRACT: Referring to R.C. Nelson's recent article on the electron

affinity of dye-desensitizers, the author points out that one of his own works, published in 1944, deals with the same subject and arrives at much the same conclusions.

There are 3 references, 1 of which is Soviet and 2 American.

ASSOCIATION: Moskva, Fiziko-khimicheskiy institut imeni L.Ya. Karpova

(The Physico-Chemical Institute imeni L.Ya. Karpov)

SUBMITTED: June 3, 1958

1. Photographic emulsions--Processing

Card 1/1

AUTHORS:

Milyutinskaya, R. I., Bagdasar yan, Kh. S., 76-32-2-29/38

Kopytovskiy, Yu.

TITLE

Investigation of the Mechanism of Radical Reactions (Issledovaniye mekhanizma radikal'nykh reaktsiy)
V. Decay of 4-Nitrobenzoylperoxide in Toluene
(V. Raspad perekisi 4-nitrobenzoila v toluole)

PERIODICAL:

Zhurnal Fizicheskoy Khimii, 1958, Vol. 32, Nr 2, pp. 428-432

(USSR).

December 15 Copy to the August 1

ABSTRACT:

Data were obtained in earlier works by the authors (reference 1) which prove the assumptions of rederence 3 concerning the scheme of the formation of diphenyl in the decomposition of nitroben=zoylperoxide and its substituents in aromatic solvents according to (1) and (2). The radical occuring in (1) and (2) can in a special case also be a benzoate radical. The there obtained result agrees with the mechanism of the formation of nitrobenzoic acid (according to reactions (1) and (2), where X denotes a nitrobenzoate radical) from reaction (3). In this connection the following problem appaers: can a nitrobenzoate radical dissolve out a movable hydrogen from the alkyl group belonging to the arom

Card 1/3

Investigation of the Mechanism of Radical Reactions V. Decay of 4-Nitrobenzoylperoxide in Toluene

76-32-2-29/38

matic ring? In order to solve this problem the authors investigated the decomposition of h-nitrobenzoylperoxide in toluene partly deuterized in the methyl group, as well as in toluene partly deuterized in the ring. The results obtained showed without any doubt two ways for the formation of nitroberzoi: acid: the reaction (3) that is R = $NO_2C_6H_{\mbox{\scriptsize h}}$, R = CH_3 , and the

reaction (4). Data are given by means of which the share of nitrobenzoic acid obtained by reaction (4) as well as the kinetic isotopic effect in this reaction can be determined. The equations (5) and (6) for the deuterium content in nitroben= zoic acid (obtained in the toluene deuterized in the ring or the methyl group) are given. From these the equation (7) for the isc= topic effect is obtained. The values calculated according to this equation are within the limits of from 1,79 to 2,17. The isotopic effect in the reaction of the dissolving out of hydrogen from the toluene by the 100_2 C6H4C00 radical (reaction (4)) is equal to 1,92.

The share of the nitrobenzoate radicals which react according to reaction (3)-in the concentration of peroxide in the solution from 0,16 M and 100° - amounts to 0,365. The work was discussed with S. S. Medvedev.

Card 2/3

Investigation of the Mechanism of Radical Reactions

76-32-2-29/38

V. Decay of 4-Nitrobenzoylperoxide in Toluene

There are 1 table, and 7 references, 2 of which are Soviet.

ASSOCIATION: Physico-ch emical Institute imeni L. Ya. Karpov, Loscow (Fiziko-khimicheskiy institut im. L. Ya. Karpova, Moskva)

SUBMITTED:

December 12, 1956.

2. Benzoyl peroxide--Decomposition 1: Nitro compounds +- Decomposition

3. Toluene--Chemical reactions

Card 3/3

AUTHORS:

Krongauz, V. A., Bagdasar'yan, Kh. S.

76-32-3-36/43

TITLE:

The Radiolysis of Solutions of Tertiary Butyl Peroxide

(Radioliz rastvorov perekisi tretichnogo butila)

PERIODICAL:

Zhurnal Fizicheskoy Khimii, 1958, Vol 32, Nr 3,

p 717 (USSR)

ABSTRACT:

It had already been shown earlier that upon γ-radiation of benzoyl solutions (in benzene), a transition of the primarily absorbed energy—excited benzene molecules to the molecules of peroxide, takes place. It is interesting to find out whether the taking up of energy of benzoyl peroxide is to be traced back to the presence of the weak peroxide bond or to the aromatic molecular structure of peroxide. In order to verify the assumption that the former is not the cause, the investigations in benzene and cyclohexane solutions mentioned in the title were performed. The concentrations of the solutions were 0.02 -0.5 mol/1; the γ-radiation was obtained by Co⁶⁰. From the small yield of the radiation was obtained by co⁶⁰. From the small yield of the radiation was concluded that no energy transfer

Card 1/2

76-32-3-36/43

The Radiolysis of Solutions of Tertiary Butyl Peroxide

from the solvent to peroxide takes place. In connection with the earlier observations, it can be maintained that especially effective transfers of excitation energy only take place in cases where both solution components possess an aromatic structure. Individual data of concentrations, as well as energetic quantities and measurements are given. There are 3 references, 1 of which is Soviet.

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova, Moskva (Moscow, Marker Land Institute imeni L. Ya. Karpov)

SUBMITTED:

February 21, 1957

Card 2/2

AUTHORS: Sinitsyna, Z. A., Bagdasar yan, Kh. S. SOV/76-32-6-20/46

TITLE: The Determination of the Velocity Constant of the Elementary

Reactions in Methylacrylate Polymerization (Opredeleniye konstant skorostey elementarnykh reaktsiy polimerizatsii

metilakrilata)

PERIODICAL: Zhurnal fizicheskoy khimii, 1958, Vol. 32, Nr 6, pp.1319-1327

(USSR)

ABSTRACT: It was found earlier that the photopolymerization of methyl-

acrylate proceeds with a constantly increasing velocity. Determinations of the reaction constants were conducted by Matheson et al. (Ref 2), Mellville et al. (Refs 3, 4), and by Mahadevan and Santhappa (Ref 5). The problem is investigated at a certain concentration of the initiator (dinitrile of azodiisofatty acid) a given length of the molecular chain, a given initiation velocity and mean life of the kinetic chains. From the experimental part may be seen among other

things that the polymerization velocity was determined by dilatometric methods. The experimental arrangement is represent-

ed schematically. The mean life of the kinetic chains was

Card 1/3 determined according to the method of intermittent illumination,

SOV/76-32-6-20/46

The Determination of the Velocity Constant of the Elementary Reactions in Methylacrylate Polymerization

by using a collection of slotted disks. The obtained functions of the logarithm of the polymerization velocity versus the logarithm of the concentration of the initiator are plotted in a graph. In the calculations the author proceed from the equation by Khauvink. Agreement is found with the data by Furman and Mesrobian (Ref 8). The initiation velocity is determined from the duration of the induction period in the presence of α,α -diphenyl- β -picryl hydrazyl. From a comparison of the initiation velocity with the decomposition velocity of the dinitrileazofatty acid the efficiency of initiation is determined. The mean life of the polymer radicals was computed from an equation which is derived from measurements carried out according to the above mentioned method at a continuous or a discontinuous illumination. From the values obtained the kinetic constants for the given case are computed. They are compared in a table with the data obtained by other authors. There are 6 figures, 4 tables, and 12 references, 5 of which are Soviet.

Card 2/3

The Determination of the Velocity Constant of the Elementary Reactions in Methylacrylate Polymerization

ASSOCIATION: Piziko-khimicheskiv institut im. L. Yr. Farnova, Moskva

(Institute of Physics and Chemistry imeni L.Ya. Karpor, Moscow)

SUBMITTED: February 9, 1957

1. Acrylic resins--Polymerization 2. Acrylic resins--Chemical reactions

Card 3/3

APPROVED FOR RELEASE: 06/06/2000 CIA-RDP86-00513R000103010011-4"

Krongauz, V. A., Bagdasar'yan, Kh. S. SOV/76-32-8-22/37 AUTHORS:

TITLE:

The Investigation of the Radiochemical Effect of the Excitation Energy Transfer in Binary Systems by Means of the Polymerization

Method (Issledovaniye radiatsionno-khimicheskogo effekta

perekhoda energii vozbuzhdeniya v dvukhkomponentnykh sistemakh

metodom polimerizatsii)

PERIODICAL:

Zhurnal fizicheskoy khimii, 1958, Vol. 32, Nr 8, pp. 1863-1868

(USSR)

ABSTRACT:

Continuing earlier papers the investigation mentioned above was carried out to further explain the corresponding problems; the authors investigated the radiation polymerization of styrene alone as well as together with methyl methacrylate in the presence of benzoyl peroxide and the dinitrile of azoiso fatty acid. The polymerization was carried out under the influence of F-rays of Co60 at 30,2°C in the dilatometer described already. The experimental results show that the addition of 0,01 mole/1 of the peroxide to styrene increases its polymerization rate by a factor of three, i. e. the formation rate of the radicals (initiating the polymerization) is increased by a factor of nine.

Card 1/3

SOV/76-32-8-22/37

The Investigation of the Radiochemical Effect of the Excitation Energy Transfer in Binary Systems by Means of the Polymerization Method

In the case of an addition of dinitrile no energy transfer from the solvent to the dissolved substance was found. This is (as in earlier papers) explained by the fact that the nitrile does not contain an aromatic ring (like the peroxide), as the role of the energy acceptor is dependent on the aromatic structure. In connection with the observations made by T. S. Nikitina and Kh. S. Bagdasar'yan (Ref 6) the time course of the common radiation polymerization of styrene and methyl methacrylate is investigated. An addition of styrene considerably decreases the polymerization rate. The starting rate is calculated according to an equation by Melville (Melvil) (Ref 12). A difference between the data obtained and those by Nikitin and Bagdasar yan is explained by a difference between the methods employed. An agreement of the data obtained with those by Walling (Voling) (Ref 9) is found. Finally the authors express their gratitude to S. S. Medvedev, Member, Academy of Sciences, USSR. There are 4 figures and 18 references, 5 of which are Soviet.

Card 2/3

SOV/76-32-8-22/37 The Investigation of the Radiochemical Effect of the Excitation Energy Transfer in Binary Systems by Means of the Polymerization Method

ASSOCIATION:

Fiziko-khimicheskiy institut im. L. Ya: Karpova, Moskva

(Physical and Chemical Institute imeni L. Ya. Karpov, Moscow)

SUBMITTED:

March 23, 1957

Card 3/3

5(4) AUTHOR:

Bagdasar'yan, Kh. S.

SOV/76-32-11-24/32

TITLE:

The Inhibiting Effect and the Structure of Inhibitors

(Ingibiruyushchiy effekt i stroyeniye ingibitorov) I. Kinetics of Inhibited Polymerization (I. Kinetika ingibirovannoy poli-

merizatsii)

PERIODICAL:

Zhurnal fizicheskoy khimii, 1958, Vol 32, Nr 11, pp 2614-2623

(USSR)

ABSTRACT:

In the present paper a method suggested already earlier by the author (Ref 1) is further developed for the investigation of the subject mentioned in the title. The described method serves for the analysis of kinetic data of inhibited polymerizations and is similar to the method by Kice (Kays) (Ref 2), so that by some modifications of the final equation the equation mentioned by Kice may be obtained. The method makes possible a good classification of the function of the inhibition reaction

versus the concentration of the inhibition. Moreover, the values q and λ_x (q = coefficient of the "regeneration" of the reaction

Card 1/2

chain) can be determined for various values of the inhibitor. The values $\alpha,~q$ and λ_x were calculated for two different inhibitor

The Inhibiting Effect and the Structure of Inhibitors. I. Kinetics of In-, hibited Polymerization

> concentrations in polymerizations of methacrylate (Ref 6), methyl methacrylate (Ref 2), and vinyl acetate (Ref 3); they are given in a table (Table 1). It was found that the interesting conclusions on secondary reactions in the case of an inhibition may be obtained from a comparison of the kinetic data and the length of the polymer chains. The inhibiting mechanism apparently consists (in vinyl acetate by isopropy] benzene) in a separation of the mobile hydrogen atom from the isopropyl benzene molecule by a polymer radical. Corresponding to the obtained data (Table 1) the formed dimethyl-phenylmethyl radical reacts with the polymer radical. There are 4 figures, 2 tables, and 6 references, 3 of which are Soviet.

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova Moskva (Physico-Chemical Institute imeni L. Ya. Karpov, Moscow)

SUBMITTED:

May 30, 1957

Card 2/2

5(4)

AUTHORS:

Sinitsyna, Z. A., Bagdasar'yan, Kh. S. SOV/76-32-12-2/32

TITLE:

The Inhibiting Effect and the Structure of Inhibitors (Ingibiruyushchiy effekt i stroyeniye ingibitorov) II. The Inhibited Polymerization of Methyl Acrylate (II. Ingibirovannaya

polimerizatsiya metilakrilata)

PERIODICAL:

Zhurnal fizicheskoy khimii, 1958, Vol 32, Nr 12,

pp 2663 - 2672 (USSR)

ABSTRACT:

A study was made of hydrocarbons with an unstable hydrogen atom, hydrocarbons with condensed or conjugate rings and nitro-compounds. The reactivity was compared with the hydrocarbons in which deuterium was substituted. R. I. Milyutinskaya determined the deuterium content. Because of contradictory results it was not possible to determine whether the formation of polymers was by disproportionation or combination of polymer radicals. In the case of hydrocarbons with an unstable H-atom the cooperation of the latter in the polymerization process has been confirmed: triphenyl deutero-methane has a weaker effect than triphenyl methane. - Fluorene and triphenyl methane have an inhibiting effect whereas diphenyl methane,

Card 1/3

The Inhibiting Effect and the Structure of Inhibitors. SOV/76-32-12-2/32 II. The Inhibited Polymerization of Methyl Acrylate

dibenzyl and toluyl nitrile are ineffective. With condensed or conjugate ring hydrocarbons the effect decreases rapidly from anthracene to phenanthrene and stilbene; naphthalene, diphenyl, m-diphenyl-benzene and quinoline are ineffective. This gradation corresponds to the series found by M. Szwarc (Ref 12). Amines and phenols (phenol, aniline, diphenyl amine, diphenyl ether, hydroquinone, triphenyl carbinol) have no inhibiting effect α -naphthol inhibits, but naphthalene and α-fluoronaphthalene do not. All nitro-compounds inhibit. The effect of further substituents is in accordance with Hammett's rule, Hammett's constant & being 0.8. Nitrobenzene and nitrodeutero-benzene are equally effective. A polymerization by the transition of an H-atom from the phenyl ring to the polymeric radical does not take place in this case. C. Price (Ref 14) assumed a binding of the polymeric radical to the phenol ring with a simultaneous formation of an inactive radical. Bartlett and Hammond (Ref 16) assumed a binding of the polymeric radical to an O-atom of the nitro-group. However, the partial reduction of the nitro-group and polymerization by disproportionation is also possible. Polyani's rule on the

Card 2/3

The Inhibiting Effect and the Structure of Inhibitors. SOV/76-32-12-2/32 II. The Inhibited Polymerization of Methyl Acrylate

effect of electron-acceptor substituents on the reaction heat was confirmed. With all inhibitors studied one molecule interrupts two kinetic chains. - Professor S. S. Medvedev cooperated in an advisory capacity. There are 3 figures, 3 tables, and 17 references, 6 of which are Soviet.

ASSOCIATION:

Fiziko-khimicheskiy institut im. L. Ya. Karpova Moskva (Physico-Chemical Institute imeni L. Ya. Karpov, Moscow)

May 30, 1957 SUBMITTED:

Card 3/3

PHASE I BOOK EXPLOITATION

sov/2649

5(3)

Bagdasar'yan, Khristofor Stepanovich

Teoriya radikal'noy polimerizatsii (Theory of Radical Polymerization) Moscow, Izd-vo AN SSSR, 1959. 297 p. Errata slip inserted. 4,000 copies printed.

Sponsoring Agency: Akademiya nauk SSSR. Institut nauchno-tekhnicheskoy informatsii.

Ed.: S.S. Medvedev, Academician; Ed. of Publishing House: A.L. Bankvitser; Tech. Ed.: I.F. Kuz'min.

PURPOSE: This book is intended for scientists working in the field of polymer chemistry.

COVERAGE: This monograph reviews the present state of the theory of radical polymerization in connection with the general theory of radical reactivity.

The first part of the book covers the chemistry of elementary reactions and their kinetic characteristics and the polymerization kinetics and length of polymeric chains formed under different conditions. The second part discusses

Card 1/8

Theory of Radical Polymerization	sov/2649
PART I. KINETICS AND MECHANISM OF PO	OLYMERIZATION -
Ch. I. Polymerization Kinetics and the Mean Length of 1. General characteristics of elementary reactions 2. General characteristics of polymerization kinetic 3. Initial stationary rate of polymerization 4. Mean length of polymeric chains 5. Distribution function for polymeric molecules 6. Determination of Pn from the viscosity of polymeric 1. Methods for determining rates and efficiencies 2. The theory of primary recombination 3. Initiation mechanism in solutions 4. Initiation with benzoyl peroxide 5. Initiation with azo compounds 6. Redox initiation 7. Initiation with systems: benzoyl peroxide - and 8. Thermal initiation 9. Photochemical initiation	Polymeric Chains 5 5 9 ics 9 11 15 19 24 of initiation 29 32 35 38 49 51

sov/2649	
Theory of Radical Polymerization	127
3. Intramolecular segment distribution	130
4. Kinetics of copolymerization	-
	136
Ch. V. Chain Transfer and Inhibition Reactions	136
1. General classification 2. Kinetics of inhibited polymerization. Presence of an efficient inhibit	138
2. Kinetics of inhibited polymera	142
in very small quantities in very small quantities	
origin of induction periods Kinetics of inhibited polymerization. Inhibitors with low efficiency Kinetics of inhibited polymerization.	143
nregent in large quantitation and the chain transfer reactions	149
present in large quantities present in large quantities Mean length of polymeric chains in chain-transfer reactions Chemistry of the reactions of chain transfer and inhibition	154
Ch. VI. Rate of Polymerization and the Length of Polymeric Chains in Exten-	167
ch. VI. Rate of formation sive Polymerization	167
on the growth and termination reactions	171
2. Chain transfer reactions	173
z Vinetics and mechanism of the first	
PART II, SOME PROBLEMS IN THE THEORY OF RADICAL REACTIVITY	
PART 114	
Card 5/8	
VIII - 11 -	

APPROVED FOR RELEASE: 06/06/2000 CIA-RDP86-00513R000103010011-4"

Sov/2649	
Theory of Radical Polymerization	225
 Addition of radicals to aromatic rings Addition of radicals to quinones 	232
	236
Ch. XI. Relative Radical Reactivity	
OHe Wie Home	242
Ch. XII. Polar Effects in Radical Reactions	242
1. General concepts	249 256
2. Application of the name of catalogue and a complyment zation reactions	250 260
7. Polar effect in copolymerical constants	
Ch. XIII. Quantum-Chemical Methods for the Qualitative Interpretation of	5/5
Ch. XIII. Quantum-Chemical Methods for the quantum-Chemical Methods	265 265
Radical Resculator	268
1. Localization energy 2. Free-valence indices	271
- · · · · · · · · · · · · · · · · · · ·	272
h Method of conjugation coefficients	276
m multiple method	lander
Addenda. Application of the Method of Molecular Orbits to Molecules With	conju- 281
gate Bonds	
Card 7/8	

,5(4); 21(8)

507/20-127-5-32/58

AUTHORS:

Krongauz, V. A., Bagdasar'yan, Kh. S.

TITLE:

The Transfer of Excitation Energy and the Sensitization of Chemical Reactions in the Radiolysis of Solutions of Aromatic

Azocompounds

PERIODICAL:

Doklady Akademii nauk SSSR, 1959, Vol 127, Nr 5, pp 1047-1050

(USSR)

ABSTRACT:

In preceding papers (Refs 1,2) the authors investigated the radiolysis of benzoyl peroxide dissolved in benzene, and found a considerable sensitization to occur. The decay rate of benzoyl peroxide was twenty times as high as corresponded to the direct action of the radiation. It was concluded herefrom that the solvent transfers energy on to the dissolved substance. According to reference 6, small additions of phenanthrene and

anthracene decrease the velocity of the radiolysis, because (Ref 7), they are also energy acceptors. For the purpose of investigating the influence of the structure of the dissolved substance on the energy transfer, the radiolysis of the following aromatic azocompounds was carried out: Phenylazotriphenyl

Card 1/3

methane (PhATM), diazosminobenzene, benzylphenyl triazene, and methyl-

SOV/20-127-5-32/58
The Transfer of Excitation Energy and the Sensitization of Chemical Reactions in the Radiolysis of Solutions of Aromatic Azocompounds

phenyl triazene. Radiclysis was carried out by means of & rays of Co60 in solutions from which ar had been carefully removed. The primary yield of decay products per 100 ev of absorbed energy was determined. Figure 1 shows the course taken by the radiolysis of PhATM . The yield in decay products increases rapidly up to a PhATM concentration of 0.01 mol/l, after which it becomes linear. This course, which proves a more intense decay of PhATM than would correspond to radiation, confirms the opinion that benzene transfers its excitation energy to PhATM. The radiolysis of benzoyl peroxide is considerably hampered by the addition of PhATM, which is proof of the fact that the latter is just as active an energy acceptor as benzoyl peroxide. DAB, BPhT, and MPhT do not decay with noticeable velocity under the action of A-rays (Table 1). In the case of azobenzene a transisomerization which increases linearly with irradiation (Fig 2) occurs during irradiation. The results obtained prove that, between the structure of the molecule and its ability of taking up the energy of electron excitation and utilizing it for the carrying out of chemical reactions, there is no direct connection. There are 2 figures, 2 tables, and

Card 2/3

APPROVED FOR RELEASE: 06/06/2000 CIA-RDP86-00513R000103010011-4"

sov/20-127-5-32/58

The Transfer of Excitation Energy and the Sensitization of Chemical Reactions in the Radiolysis of Solutions of Aromatic Azocompounds

13 references, 8 of which are Soviet.

ASSOCIATION: Nauchno-issledovatel skiy fiziko-khimicheskiy institut im.

L. Ya. Karpova (Physico-chemical Scientific Research Institute

imeni L. Ya. Karpov)

PRESENTED:

April 15, 1959 by S. S. Medvedev, Academician

SUBMITTED:

April 11, 1959

Card 3/3

68348

5.5500 5(4) authors:

Bagdasar'yan, Kh. S., Wilyutinskaya, R. I. S/076/60/034/01/043/044 B004/B007

TITLE:

A New Method of Investigating the Reactivity of Organic Compounds to Radicals

PERIODICAL:

Zhurnal fizicheskoy khimii, 1960, Vol 34, Nr 1, pp 234 - 235 (USSR)

ABSTRACT:

The authors describe a variant of the method of competitive reactions, which was worked out by themselves. It is based upon the application of tagged radicals and the determination of the reaction products by means of isotope dilution. Thus it is possible to use the tagged radicals in low concentration (0.01 ml/l), so that the reactions of these radicals may be neglected. The authors describe carrying-out of their method in the case of the reaction of the phenyl radical with aromatic compounds. A table gives the data for the reaction of benzoyl peroxide in a mixture of benzene + CCl₄, nitrobenzene + CCl₄, naphthalene + CCl₄, and cumene + CCl₄ at 100°.

Card 1/2

68348

A New Method of Investigating the Reactivity of S/076/60/034/01/043/044 Organic Compounds to Radicals B004/B007

The reaction constants found agree with the data obtained by employing other methods. At present the authors employ the method described for systematic investigations. There are 1 table and 3 references, 1 of which is Soviet.

 $\sqrt{}$

ASSOCIATION:

Fiziko-khimicheskiy institut im. L. Ya. Karpova Moskva

(Institute of Physical Chemistry imeni L. Ya. Karpov, Moscow)

SUBMITTED:

June 18, 1959

Card 2/2

3.3200 68856 5/076/60/034/02/021/044 5.3830(A) Milyutinskaya, R. I., Bagdasar'yan, B010/B017 AUTHORS: Kh. S. Investigation of the Mechanism of Radical Reactions. VI. On the Reaction Mechanism of Benzoyl Peroxide With Amines TITLE: Zhurnal fizicheskoy khimii, 1960, Vol 34, Nr 2, pp 405-412 (USSR) PERIODICAL: S. P. Gambaryan (Refs 1,2) had already observed that amines react rapidly with benzoyl peroxide. O. A. Chaltykyan (Ref 4) and Horner ABSTRACT: (Ref 5) found that free radicals are formed in this connection. Since the reaction kinetics proper has been little investigated the authors tried in the present case, in centinuation of previous investigations (Ref 7), to obtain a direct proof of the formation of free radicals in the reaction of benzoyl peroxide with secondary amines. The polymerization method and the reaction with diphenylpicrylh, razine were applied, and the kinetic isotope effect in the exchange of the hydrogen atoms in the amino group with deuterium was determined. N-deuterium aniline and N-deuterium diphenylamine were produced by shaking out with heavy water, &, &'-diphenyl-\$picrylhydrazine (DPPH·H) and the corresponding hydrazyl (DPPH) was produced by E. A. Mistryukov according to the method of Renn-Goldschmidt (Ref 8). The polymerization kinetics of methyl-Card 1/3

Investigation of the Mechanism of Radical Reactions. VI. On the Reaction Mechanism of Benzoyl Peroxide

68856 \$/076/60/034/02/021/044 B010/B017

methacrylate initiated by the benzoyl peroxide diphenylamine mixture was investigated according to the dilatometric method by Z. A. Sinitsyna. The value k = 1.17.10 exp (- 16400/RT) 1/mol sec. (1) was obtained for the bimolecular constant of the reaction with diphenylamine, and the value $k = 1.86 \cdot 104 exp (-10700/RT) 1/mol$ sec. (4) with aniline. A comparison of the constant of the reaction rate (Tables 1,2) shows that the constant does not change in the exchange of protium with deuterium, i.e. no isotope effect takes place, and thus the transition of hydrogen from the amine to benzoyl peroxide does not influence the reaction rate. Kinetic experiments on the reaction of benzoyl peroxide with anilines substituted in the ring have also been carried out (Table 3). The constants of the Arrhenius equation for the benzoyl-peroxide reactions with amines are mentioned (Table 4), and the reactions are discussed from the point of view of the reaction theory of electron transition. The benzoyl-peroxide reaction with diphenylamine takes place clearly with the formation of free radicals which are capable of cleaving off the hydrogen atom from DPPH. H, and which effect a polymerization of methylmethacrylate. The efficacy of the benzoyl peroxide diphenylamine mixture in bringing about the polymerization

Card 2/3

With Amines

68856

Investigation of the Mechanism of Radical Reactions. VI. On the Reaction Mechanism of Benzoyl Peroxide

s/076/60/034/02/021/044 B010/B017

With Amines

of methylmethacrylate was found to be about 0.001 at 250. A paper by A. S. Kuz'minskiy and L. G. Angert is mentioned in the text. There are 4 figures, 4 tables, and 19 references, 9 of which are

Soviet.

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova Moskva (Institute

of Physical Chemistry imeni L. Ya. Karpov, Moscow)

SUBMITTED:

May 12, 1958

Card 3/3

S/076/60/034/05/28/038 B010/B003

5.3831

Sinitsyna, Z. A., Bagdasar'yan, Kh. S.

AUTHORS: TITLE:

The Inhibiting Effect and the Structure of Inhibitors.

III. Inhibited Polymerization of Vinyl Acetate \

PERIODICAL:

Zhurnal fizicheskoy khimii, 1960, Vol. 34, No. 5,

pp. 1110-1116

TEXT: Continuing a previous paper the authors investigated the inhibited polymerization of vinyl acetate. They measured the initial rate of polymerization in the presence of different inhibitors, and determined the mean length of the polymeric chains viscosimetrically. Data on the polymerization of vinyl acetate (at 50°C; concentration of the monomer of 10.5 moles/l; initiator: azoisobutyric acid dinitrile) are given in Table 1. The rate of initiation was determined with diphenylpicrylhydracil (Fig. 2), and the induction period was measured (Table 2). Table 3 gives experimental data on the inhibition of the polymerization of vinyl acetate at 50° in the presence of 1.7°10⁻² moles/l of azoiso-

7 Card 1/2

The Inhibiting Effect and the Structure of Inhibitors. III. Inhibited Polymerization of Vinyl Acetate

S/076/60/034/05/28/038 B010/B003

JU1 . 1

butyric acid dinitrile by different inhibitors. The authors found that each molecule of the inhibitor tears two kinetic chains, and that the latter are not regenerated. Each chain forms a polymeric molecule. Substituents of electron donors and acceptors increase the reactivity of the phenyl ring with respect to the polyvinylacetate radical, i.e., they increase the effect of the inhibitor. The quantity $k_{\rm x}/k_{\rm p}$ for nitrobenzene is higher by 3 orders of magnitude than that for other benzene derivatives. As already found in the polymerization of methylacrylate, the effect of substituents in nitrobenzene obeys the Hammett law ($\xi=0.76$). The reactivity of the polyvinylacetate radical exceeds that of the polymethylacryl radical by 3-4 orders of magnitude. The authors established that $k_{\rm p}/k_{\rm o}^{-1/2}=0.275$ for vinyl acetate at 50°C. A scheme for the reaction between polymeric radicals, benzene derivatives, and hydrocarbons is suggested. There are 4 figures, 3 tables, and 16 references: 6 Soviet, 8 American, and 2 British.

SUBMITTED:

July 23, 1958

Card 2/2

APPROVED FOR RELEASE: 06/06/2000 CIA-RDP86-00513R000103010011-4"

4

S/076/60/034/007/021/042/XX B004/B068

AUTHOR:

Bagdasar'yan, Kh. S.

TITLE:

Relative Reactivity of Radicals

PERIODICAL:

Zhurnal fizicheskoy khimii, 1960, Vol. 34, No. 7,

pp. 1517-1523

TEXT: In this paper, the following problem is discussed: Hitherto, no experimental method has been available for the direct determination of the relative reactivity of different radicals with a molecule having saturated valences. Only a comparison of the absolute rate constant or activation energy is possible, the experimental determination of which is difficult. An equation for an indirect comparison of the reactivities of radicals with a number of saturated molecules was suggested by Szwarc and others (Ref. 1):

others (Ref.1): $\log(k_{R_1^{A_i}}/k_{R_1^{A_0}}) = n \log(k_{R_2^{A_i}}/k_{R_2^{A_0}})$ (1),

where $k_{R_1A_1}$ is the rate constant of the reaction of radical R_1 with the

Card 1/4

Relative Reactivity of Radicals

S/076/60/034/007/021/042/XX B004/B068

molecule Λ_i . The meaning of the constants k with the remaining subscripts is analogous; Λ_o is the molecule used as standard; n is a constant. On the basis of experimental data on the reactions of polyvinyl acetate and polymethyl acrylate radicals with aromatic nitro-compounds it is shown that the value n in equation (1) has no physical significance and is not constant either. The possible physical significance of n is investigated. If the free activation energy ΔF^F (equation 4) is used instead of the rate constants k in equation (1), with $\Delta F^F = E - T\Delta S^F$ (5), then one obtains: $(E_{R_1\Lambda_i} - E_{R_1\Lambda_o}) - T(\Delta S_{R_1\Lambda_i}^F - \Delta S_{R_1\Lambda_o}^F) = n(E_{R_2\Lambda_i} - E_{R_2\Lambda_o}) - nT(\Delta S_{R_2\Lambda_i}^F) - \Delta S_{R_2\Lambda_o}^F$ $-\Delta S_{R_2\Lambda_o}^F) \quad (6). \text{ Application of the equation } T\Delta S^F = \beta E + \gamma \quad (8) \text{ usual for liquid phases, with } \beta \text{ and } \gamma \text{ being constants for a given temperature, yields}$ $T\Delta \Delta S_{\Lambda_i\Lambda_o}^F = \beta \Delta E_{\Lambda_i\Lambda_o} \quad (9). \quad \Delta \Delta S_{\Lambda_i\Lambda_o}^F \quad \text{is the change of entropy; } \Delta E_{\Lambda_i\Lambda_o}^F \quad \text{is the change of activation energy when, in a number of similar reactions,}$ Card 2A

Relative Reactivity of Radicals

S/076/50/034/007/021/042/XX B004/B068

molecule A_i reacts instead of molecule A_o . β is a factor. Using (9), (6) is transformed to yield $(1-\beta_1)^{\Delta E}R_1^{A_iA_0} = n(1-\beta_2)^{\Delta E}R_2^{A_iA_0}$ (10). $\Delta E_{R_1A_iA_0}$ is the difference between the activation energy of the reaction of radical R_1 with A_i and the activation energy of R_1 with A_0 . β_1 and β_2 are the β -values (from equation 9) for the reactions with the radicals R_1 and R_2 . The activation energy $E_{R_1A_i}$ can also be calculated from the difference between the energies of the initial and the transition state: $E_{R_1A_i} = U_{R_1A_i}^{k} - (U_{R_1} + U_{A_i}), \quad (11) \quad (U_{R_1A_i}^{k})$ is the transition-state energy; $U_{R_1}, U_{A_i} = U_{R_1A_i}^{k} - U_{R_1A_i}^{k} - U_{R_1A_i}^{k}$ The following equation is obtained: $(U_{R_1A_i}^{k} - U_{R_1A_i}^{k})/(U_{A_i} - U_{A_i}) - 1 = n[(1 - \beta_2)/(1 - \beta_1)] \left[(U_{R_2A_i}^{k} - U_{R_2A_o}^{k})/(U_{A_i} - U_{A_o}) - 1 \right] \quad (12)$. The fractions Card 3/4

Relative Reactivity of Radicals

S/076/60/034/007/021/042/XX B004/B068

containing U indicate the ratio of the variation of the energy level of the transition state to the variation of the energy level of the initial state for the transition from molecule A_0 to molecule A_1 , and are defined as the "susceptibility" of the reaction of a given radical (or ion) to the structure factor (e.g., a substituent) within the series of a given type of molecule. If δ_{R_1} , δ_{R_2} are introduced for this susceptibility, one obtains: $n(1-\beta_2)/(1-\beta_1) = (\delta_{R_1}-1)/(\delta_{R_2}-1)$ (13). If β_1 becomes equal to β_2 , especially if $\beta_1 = \beta_2 = 0$ (isentropic reaction), n is the relative

susceptibility of the reaction under participation of radicals R, and R2 to the structure factor of a general series of molecules with which the radicals react. In the general case, however, n (as well as Hammett's constant) has no simple physical significance. There are 2 figures and 12 references: 5 Soviet, 4 US, 1 British, and 2 Canadian.

ASSOCIATION:

Fiziko-khimicheskiy institut im. L.Ya. Karpova (Physico-

chemical Institute imeni L. Ya. Karpov)

SUBMITTED:

September 29, 1968

Card 4/4

S/020/60/132/05/45/069 B004/B011

5.4500(B)

AUTHORS:

Krongauz, V. A., Bagdasar'yan, Kh. S.

TITLE:

Excitation Energy Transfer and Sensitization of Chemical Reactions in the Radiolysis of Organic Disulfide Solutions

PERIODICAL:

Doklady Akademii nauk SSSR, 1960, Vol. 132, No. 5,

pp. 1136-1139

TEXT: The authors found in previous investigations (Refs. 1, 2) that highly reactive substances in benzene solution gave a higher radiation yield than corresponded to the direct action of radiation, and therefore they concluded upon a transfer of excitation energy by benzene. Here, these investigations are continued for diphenyl disulfide, dibenzyl disulfide, and dibenzoyl disulfide. To prevent the radicals from recombining, diphenyl picryl hydrazyl was added. Radiolysis was carried out by means of gamma radiation of Co⁶⁰. The radiation yield per 100 ev was determined by measuring the reduction in concentration of diphenyl picryl hydrazyl with the aid of an Co⁶⁰. SF-4) spectrophotometer. Fig. 1 shows the experimental results which confirm the energy transfer. Fig. 2

Card 1/3

Excitation Energy Transfer and Sensitization of Chemical Reactions in the Radiolysis of Organic Disulfide Solutions

S/020/60/132/05/45/069 B004/B011

illustrates the linear dependence of the disulfide decomposition on concentration. Equation (1) is written down for the quantity of the resulting decomposition products, taking account of the following constants: k_1 - rate of formation of excited benzene molecules, k_2 - rate of their de-activation, k_1^* rate of energy transfer, k_1^* and k_2^* rate of de-activation and dissociation of excited disulfide molecules. Table 1 specifies the values for k_1^*/k_2 and $k_1^*k_2^*/(k_4^*+k_2^*)$. At least 2 excited benzene molecules are formed every 100 ev. The CH₂ group does not

prevent the energy from migrating to the S-S group, as is confirmed by equal values for diethyl disulfide and dioctyl disulfide. Furthermore, the authors studied the action of the benzoyl peroxide addition. As is shown in Fig. 3, the decomposition of benzoyl peroxide decreases with a rising disulfide concentration, with the dibenzoyl disulfide exerting a stronger protective action. Fig. 4 shows that there is no linear dependence of the resulting decomposition products on concentration but a dependence according to equation (3). The strong protective action of

Card 2/3

W

Excitation Energy Transfer and Sensitization of Chemical Reactions in the Radiolysis of Organic Disulfide Solutions

S/020/60/132/05/45/069 B004/B011

dibenzoyl disulfide is not clarified as yet. A. N. Silant'yeva assisted in the experiments. The authors thank V. N. Vasil'yeva for supplying the disulfide materials. There are 4 figures, 1 table, and 6 references: 4 Soviet, 1 British, and 1 American.

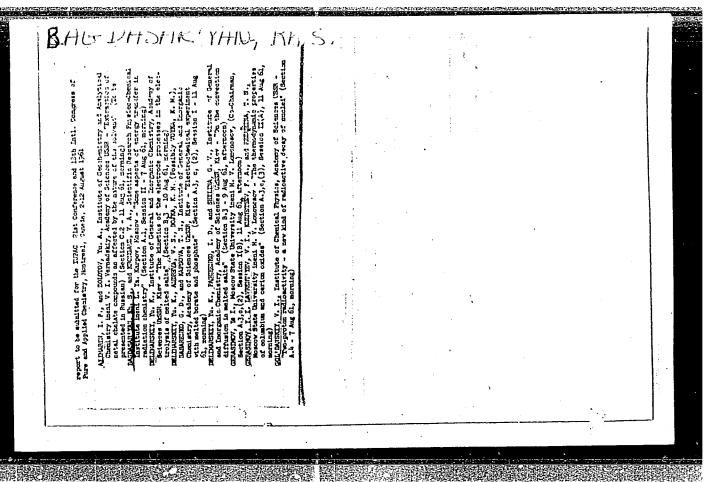
ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova (Physicochemical Institute imeni L. Ya. Karpov)

PRESENTED: February 6, 1960, by S.S. Medvedev, Academician

SUBMITTED: February 6, 1960

W

Card 3/3



BAGDASAR'YAN, Kh. S.

PHASE I BOOK EXPLOITATION

sov/4983

International symposium on macromolecular chemistry. Moscow, 1960.

Mezhdunarodnyy simpozium po makromolekulyarnoy khimii, SSSR, Moskva, 14-18 iyunya 1960 g; doklady i avtoreferaty. Sektsiya II. (International Symposium on Marromolecular Chemistry Held in Moscow, June 14-18; Papers and Summaries) Section II. [Moscow, Izd-vo AN SSSR, 1960] 559 p. 5,500 copies printed.

Sponsoring Agency: The International Union of Pure and Applied Chemistry, Commission on Macromolecular Chemistry

Tech. Ed.: T.A. Prusakova.

PURPOSE: This book is intended for chemists interested in polymerization reactions and the synthesis of high-molecular compounds.

COVERAGE: This is Section II of a multivolume work containing papers on macromolecular chemistry; The papers in this volume treat mainly the kinetics of various polymerization reactions initiated by different catalysts or induced by radiation. Among the research techniques discussed are electron paramagnetic Card 1/12

36422 s/137/62/000/003/008/191 A006/A101

24.7100

Bagadasarpa, Kh. S., Berezhkova, G. V., Kapustin, A. P.

AUTHORS: TITLE:

On the problem of growing single-crystals of zinc in an ultrasonic

field

PERIODICAL:

Referativnyy zhurnal, Metallurgiya, no. 3, 1962, 19, abstract 3A101 (V sb. "Primeneniye ul'traakust. k issled. veshchestva", no. 12,

Moscow, 1960, 41-44)

TEXT: Zn single-crystals were grown by the Bridgeman method in sealed glass tubes of 3 - 4 mm in diameter. After melting the upper portion of the crystal, the ultrasonic oscillator was switched on. The displacement speed of the single crystal in the furnace was 37 mm/hour. The test temperature was 520°C. Specimens, 7 - 8 mm high, were prepared from the grown crystals to determine compresmens, 7 - 8 mm high, were prepared from the grown crystals, grown in an sive strength. It was established that the strength of crystals, grown in an ultrasonic field, increases considerably; for instance, the elastic limit is ultrasonic field, increases considerably; for instance, the elastic limit is raised by about a factor of 6 as compared to a crystal grown without application of an ultrasonic field. An investigation of specimens annealed at 350°C, grown in an ultrasonic field, and of specimens which had been merely subjected to

Card 1/2

"APPROVED FOR RELEASE: 06/06/2000

CIA-RDP86-00513R000103010011-4

S/137/62/000/003/008/191 A006/A101

On the problem of growing ...

ultrasound, shows that the strengthening effect is removed only in the latter case. In the former specimens, the presence of a great amount of domain boundaries in the crystals proves that in these crystals the dislocation density is higher than in crystals which had been grown without applying an ultrasonic field.

T. Kolesnikova

[Abstracter's note: Complete translation]

Card 2/2

S/195/60/001/004/003/015 B017/B055

AUTHOR:

Bagdasar'yan, Kh. S.

TITLE:

Theory of Reactivity of Radicals. I. New Interpretation of

the Polar Effect in Copolymerization

PERIODICAL:

Kinetika i kataliz, 1960, Vol. 1, No. 4, pp. 503-509

TEXT: A new method differing from the Price theory was suggested, which takes into consideration the effect of conjugation and the polar effect in radical reactions. Equations for the calculation of rate constants were derived. The following equation (2) is given for calculating the activation energy: $E = A + \alpha T (\Delta E_1 + \Delta E_2)$, where A is a constant, ΔE_1 and ΔE_2 .

are the localization energies for the atoms 1 and 2 in the radical and monomer and α^r is a factor varying between 0 and 1. Fig. 1 shows the rate constant of the addition reaction of the radicals to the double bonds as a function of the sum of localization energies at 60°C. In reactions of radicals containing hetero atoms it is necessary to take into account the acceptor - donor effect in the transition state. The following equations

Card 1/3

Theory of Reactivity of Radicals. I. New Interpretation of the Polar Effect in Copolymerization

S/195/60/001/004/003/015

are given for calculating the activation energies and rate constants:

$$E = A + \alpha^{-1} (\Delta E_1 + \Delta E_2) - (x_1 - x_2)^2$$
 (5) and

 $E = A + \alpha^{\frac{1}{2}} (\Delta E_1 + \Delta E_2) - (x_1 - x_2)^2$ (5) and log $k = C - b(\Delta E_1 + \Delta E_2) + (x_1 - x_2)^2$ (6), where x_1 and x_2 are the acceptor - donor increments of the radical groups. The acceptor - donor effect at low activation energies leads to deviations from the Polyani rule. With allowance for localization energies of the electrons in the initial and final radicals, the activation energy E may be calculated from

 $E = A_{H} + \alpha_{H}^{\neq} (\Delta E_{1} - \Delta E_{2}) - a(x_{1} - x_{2})^{2}$ where A_{H} and α_{H}^{\neq} are constants. Equations 8 and 9 permit calculation of the constants of the copolymerization of r_{AB} and $r_{BA}:\log r_{AB} = -b(\Delta E_A)$ $-\Delta E_{B} - (x_{A} - x_{B})^{2}$ (8) and $\log r_{BA} = b(\Delta E_B - \Delta E_A) - (x_B - x_A)^2$ (9), where A and B are the monomers, ΔE_{A} and ΔE_{B} the localization energies of A and B and $\mathbf{x}_{\mathtt{A}}$ and $\mathbf{x}_{\mathtt{B}}$ the acceptor - donor increments of the monomers A and Card 2/3

Theory of Reactivity of Radicals. I. New Interpretation of the Polar Effect in Copolymerization

S/195/60/001/004/003/015 B017/B055

B. The localization energies and acceptor - donor increments of monomeric and polymeric radicals are listed in Table 2. Equation (12) gives the constants for copolymerization of 3 monomers, A, B and Z:

$$\log \frac{r_{BZ}}{r_{ZB}} = \log \frac{r_{BA}}{r_{AB}} + \log \frac{r_{AZ}}{r_{ZA}}$$
 (12).

There are 2 figures, 2 tables, and 12 references: 4 Soviet.

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova

(Physicochemical Institute imeni L. Ya. Karpov)

SUBMITTED: August 1, 1960

Card 3/3

S/195/60/001/004/015/015 B017/B055

AUTHORS:

Arest-Yakubovich, A. A., Bagdasar'yan, Kh. S.

TITLE:

Moscow International Symposium on Macromolecular Chemistry

PERIODICAL:

Kinetika i kataliz, 1960, Vol. 1, No. 4, pp. 627-629

TEXT: The International Symposium on Macromolecular Chemistry was held in Moscow on June 14-18, 1960. Three questions were treated: 1) polymer synthesis, 2) polymerization- and polycondensation processes and 3) chemical transformations in polymers. A total of 170 papers and communications were read. Three papers were read at the plenary session, among them one by N. N. Semenov on reactions common to polymerization processes and to polymers with conjugate bonds. S. Ye. Bresler, E. N. Kazbekov, and Ye. M. Saminskiy reported on the chemical behavior of macroradicals formed during mechanical destruction of glassy polymers in vacuum. Kh. S. Bagdasar'yan and Z. A. Sinitsyna determined the reaction constants of reactions of polymer radicals such as, e.g., vinyl acetate, methyl acrylate, and acrylonitrile with various aromatic compounds, especially those containing nitro groups. F. Tüdes, I. Kendö and M. Azori (Hungary)

Card 1/3

Moscow International Symposium on Macromolecular Chemistry

S/195/60/001/004/015/015 B017/B055

investigated the inhibition of styrene polymerization by trinitro benzene and its derivatives. G. A. Razuvayev, L. M. Terman, V. R. Likhterov and V. S. Etlis discussed studies on the kinetics and chemical mechanism of the thermal decomposition of several peranhydrides and perester radicals in various solvents. Some 20 papers were read on the subjects of ionic and stereospecific polymerization. S. S. Medvedeva and A. P. Gantmakher reported on an investigation on the kinetics and mechanism of polymerizations under the catalytic action of organolithium compounds. A.A.Korotkov and collaborators investigated the polymerization of methyl methacrylate in toluene. K. Vesely, as well as Z. Zlamala and A. Kazda (CSSR) discussed cationic polymerization. V. Boček (CSSR) described interesting results of polymerizing propylene on $Al(C_2H_5)_3$ and mixed crystals of TiCl₃ or TiCl, with halides of metals of the groups II to VIII. B. L. Yerusalimskiy reported on the dependence of the structure of isoprene and butadiene polymers prepared with ${^C_4}{^H_9}{^M}gJ + {^C_4}{^H_9}{^1}_2{^M}g + {^Ti}{^C}{^1}_4$ as catalyst on the composition of the catalysts. V. A. Kargin and N. A. Plate showed that the polymerization mechanism depends on the nature of the solid phase and the

Card 2/3

Moscow International Symposium on Macromolecular Chemistry

S/195/60/001/004/015/015 B017/B055

monomer. Polymerization in the solid state was treated in papers by V. A. Kargin and V. A. Kabanov, A. V. Volokhina and G. I. Kudryavtseva. A. D. Abkin discussed polymerization under the action of radiation and the effect of radiation on polymers. Apart from these papers, numerous papers and communications were presented on the preparation and properties of new polymers and on various conversions in polymer chains.

SUBMITTED:

September 5, 1960

Card 3/3

MILYUTINSKAYA, R.I.; BAGDASAR'YAN, Kh.S.

Mechanisms of radical reactions. Part 6: Mechanism of the reaction between benzoyl peroxide and amines. Zhur. fiz. khim. 34 no.2:405-412 F '60. (MIRA 14:7)

 Fiziko-khimicheskiy institut im. L.Ya.Karpova, Moskva. (Benzoyl peroxide) (Amines)

S/076/60/034/012/010/027 B020/B067

AUTHORS:

Sinitsyna, Z. A. and Bagdasar'yan, Kh. S.

TITLE:

Inhibiting Effect and Structure of Inhibitors. IV.

Inhibited Polymerization of Acrylonitrile

PERIODICAL:

Zhurnal fizicheskoy khimii, 1960, Vol. 34, No. 12,

pp. 2736-2741

TEXT: In Refs. 1,2 the authors reported on the reactivity of various aromatic compounds to the polymethylacrylate. and polyvinylacetate radical by using inhibited polymerization. In this paper, the authors describe a similar study of the polyacrylonitrile radical. The initial rate of polymerization of acrylonitrile in dimethyl formamide was determined in the presence of various inhibitors and the mean chain length of the polymers formed was determined viscosimetrically. The rate of polymerization was measured dilatometrically with a degree of polymerization below 6%. Under these conditions polymerization proceeds homogeneously. All experiments were made at 50°C in vacuo. Azoisobutyric acid dinitrile was used as initiator. The polymer formed was isolated from the solution by Card 1/3

Inhibiting Effect and Structure of Inhibitors. S/076/60/034/012/010/027 IV. Inhibited Polymerization of Acrylonitrile B020/B067

adding an ether - heptane mixture (1:1). Viscosity was measured at 25° C in dimethyl formamide at different concentrations of the polymer. The results obtained are given in Table 1. They indicate that the ratic between the rate of polymerization V and the square root of the initiator concentration c is constant. Fig. 1 shows the dependence $\log[\eta]$ on M^2/V (M denotes the concentration of the monomer) while Fig. 2 shows the dependence 1/P (P denotes the mean length of the polymer chains) on V/M^2 according to the following equation:

where λ the contribution of disproportionation in the bimolecular rupture, k_g the rate constant of the chain growth, k_M and k_S the constants of the rate of chain transfer by the molecules of the monomer and the solvent, and k_S the constant of the rate of the total bimolecular rupture. Neither the rate of polymerization nor the molecular weight of the polymers were reduced by addition of diphenyl picrylhydrazine (0.0005 mole/1), aniline (0.22 mole/1), naphthalene (0.20 mole/1), phenanthrene (0.10 mole/1), m-dinitrobenzene (0.10 mole/1, and symmetric

Card 2/3

Inhibiting Effect and Structure of Inhibitors. S/076/60/034/012/010/027 IV. Inhibited Polymerization of Acrylonitrile B020/B067

trinitrobenzene (0.004 mole/1). Inhibition is observed when adding anthracene, quinone, and dimethyl aniline to the reaction. The results of these experiments are given in Table 2. The value $k_{\rm g}/k_{\rm o}^{1/2}$ for acrylenitrile, which was obtained by comparing the rate of polymerization with the rate of initiation, is 0.085 at 50°C. Table 3 gives the values $k_{\rm g}/k_{\rm g}$, ($k_{\rm g}/k_{\rm g}$) denotes the constant of the reaction rate of the polymer radical with the inhibitor molecule) and $k_{\rm g}/k_{\rm g}$ for some inhibitors at 50°C. In the absence of the polarity effect, the values of the constant $k_{\rm g}/k_{\rm g}/k_{\rm g}$ decrease in all inhibitors in the same order. There are 2 figures, 3 tables, and 17 references: 8 Soviet, 7 US, and 2 German.

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova, Moskva (Physico-chemical Institute imeni L. Ya. Karpov, Moscow)

SUBMITTED: March 14, 1959

Card 3/3

36520 s/081/62/000/006/017/117 B166/B101

J. > YOO AUTHORS:

Bagdasar'yan, Kh. S., Milyutinskaya, R. I., Trosman, E. A.,

Borovkova,, V. A.

TITLE:

Quantitative studies of radical reactivity by the competitive

reaction method

PERIODICAL:

Referativnyy zhurnal. Khimiya, no. 6, 1962, 53, abstract 6B360 (Tr. po khimii i khim. tekhnol. Gor'kiy no. 1, 1961,

12 - 17)

TEXT: Using a method described earlier (RZhKhim, 1960, no. 24, 96341), measurements were made of the relative rates of attachment of phenyl radicals to aromatic rings (rate constant k_1) and of the separation rates of hydrogen from alkyl benzenes by phenyl radicals (constant k_2). Separation of chlorine from carbon tetrachloride was taken as the standard reaction (constant k_3). The following values of the constants were obtained at 100° C (the first figure is k_1/k_3 , the second figure is k_2/k_3): benzene Card 51/2

S/081/62/000/006/017/117
Quantitative studies of radical... B166/B101

0.235; -; nitrobenzene 1.0; 0.1; naphthalene 5; 0; toluene 0.48; 0.33; isopropyl benzene 0.98; 0.85; polystyrene 0.62; 0.06. The polar substitutes - the electron-donor and electron-acceptor -- activate the phenyl rings. There is no marked separation of hydrogen from the aromatic rings. The rate of hydrogen separation from the alkyl groups of polystyrene is considerably lower than it is from isopropyl benzene, which is apparently attributable to the steric factor. [Abstracter's note: Complete translation.]

 $A \cap$

50

Card 2/2

"APPROVED FOR RELEASE: 06/06/2000 CIA-RDP86-00513R000103010011-4

BAGDASAR YAN, Kh.S.

Energy of formation of a free benzoate radical. Zhur.fiz. khim. 35 no.8:1774-1776 Ag '61. (MIRA 14:8)

1. Fiziko-khimicheskiy institut imeni L.Ya. Karpova, Moskva. (Benzoic acid) (Radicals (Chemistry)) (Thermochemistry)

20209 \$/076/61/035/010/008/015 B106/B101

5.3830

AUTHORS:

Bagdasar'yan, Kh. S., and Borovkova, V. A.

TITLE:

Relative reactivity of vinyl monomers to the benzoate radical

PERIODICAL: Zhurnal fizicheskoy khimii, v. 35, no. 10, 1961, 2306 - 2310

TEXT: In a previous paper, one of the authors together with R. I. Milyutinskaya developed a method for determining the relative reactivity of vinyl monomers to the benzoate radical (Ref. 1: Kh. S. Bagdasar'yan, R. I. Milyutinskaya, Zh. fiz. khimii, $\underline{27}$, 420, 1953). This method is based on the ability of the benzoate radical to form a phenyl radical and a molecule of carbon dioxide: $PhCOO^* \longrightarrow Ph^* + CO_2$ (1). In the presence of a vinyl monomer, a competing reaction, the addition of the benzoate radical to the double bond of the monomer, takes place: $PhCOO^* + M \longrightarrow PhCOOM^*$ (2). By determining the CO_2 yield in the presence and absence of the monomer, the ratio k_2/k_1 of the reaction constants is obtained which is characteristic of the reactivity of the monomer to the benzoate radical Card 1/5

26289 S/076/61/035/010/008/015 B106/B101

Relative reactivity of vinyl monomers

(Ref. 2: R. I. Milyutinskaya, Dis. In-t im. L. Ya. Karpova, M., 1958; Ref. 3: Kh. S. Bagdasar'yan, Teoriya radikal'noy polimerizatsii (Theory of radical polymerization). Izd-vo AN SSSR, M., 1959). In the present paper, reactions of benzoate radicals with styrene and methyl methacrylate are examined by the same method at various temperatures. In addition, the values of k2/k1 for ~-methyl styrene and stilbene were determined, which practically do not homopolymerize according to the radical mechanism. The values of k2 for the latter two compounds were compared with the corresponding values of the typical monomers, styrene and methyl methacrylate. In the investigations, the CO2 yields were determined during the thermal decomposition of benzoyl peroxide in a mixture of carbon tetrachloride or benzene and the substance to be examined. The yields of benzoic acid and the resulting polymer were also determined. For the ratio k_2/k_1 , the following values were obtained at 100°C: for styrene 1.35 liters/mole, for d-methyl styrene 1.33 liters/mole, for methyl methacrylate 0.20 liters/mole, and for stilbene 2.10 liters/mole. These values increase with decreasing temperature. From this temperature dependence the Card 2/5

X.

28289

Relative reactivity of vinyl monomers ...

S/076/61/035/010/008/015 B106/B101

difference of the activation energies of reactions (1) and (2) was determined. It is 7.3 kcal/mole for styrene in carbon tetrachloride. The values of k_2/k_1 indicate that the reactivity of the double bond in

∞-methyl styrene is equal to that in styrene, and (referred to 1 reaction center 1.05 liters/mole) somewhat lower in stilbene. The fact that, in spite of this high reactivity of double bonds in ∞-methyl styrene and stilbene, no homopolymerization occurs at high temperatures is explained by the low activation energy and the resultant high reaction rate of depolymerization. The low activation energy of depolymerization is due to steric hindrances. The considerable amount of benzoic acid produced by the decomposition of benzoyl peroxide in the presence of ∞-methyl styrene or stilbene is evidently formed according to the following mechanism (e.

g., for stilbene): $Ph^{\bullet} + Ph-CH=CH-Ph \longrightarrow \frac{Ph}{Ph} > CH-\dot{C}H-Ph$ (4),

Ph CH-CH-PhCOO \longrightarrow PhCOOH + $\stackrel{Ph}{Ph}$ C=CH-Ph (5). Radicals being more readily added to double bonds than to the benzene nucleus, the reaction PhCOO + Ph-CH=CH-Ph \longrightarrow $\stackrel{PhCOO}{Ph}$ CH-CH-Ph (6) is possible instead of (4). Card 3/5

28239 S/076/61/035/010/008/015 B106/B101

Relative reactivity of vinyl monomers ...

Authors also examined the decomposition rate of benzoyl peroxide in benzene and carbon tetrachloride medium in the presence of styrene or methyl methacrylate (Table 2). Decomposition of benzoyl peroxide in the presence of styrene or methyl methacrylate proceeds at a lower rate in carbon tetrachloride than in benzene. This difference is even increased by rising temperature. At 100°C, the decomposition rate of benzoyl peroxide in benzene in the presence of styrene is considerably higher than in the presence of methyl methacrylate whereas at lower temperatures (60°C) the decomposition rates in the presence of styrene and in the presence of methyl methacrylate are of the same order of magnitude. There are 4 figures, 2 tables, and 12 references: 5 Soviet and 7 non-Soviet. The three most recent references to English-language publications read as follows: C. Barson, J. Bevington, D. Eaves, Trans. Faraday Soc., 54, 1678, 1958; J. Bevington, J. Toole, J. Polymer Sci., 28, 413, 1958; C. Barson, J. Bevington, 4, 147, 1958.

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova (Physico-chemical Institute imeni L. Ya. Karpov)

Card 45

32305 S/020/61/141/004/011/019 B101/B110

5.4600

AUTFORS:

Bagdasar yan, Kh. S., Izrailevich, N. S., and Krongauz, V. A.

TITLE:

Intramolecular transfer of energy by radiolysis of alkyl

benzenes

PERIODICAL: Akademiya nauk SSSR. Doklady, v. 141, no. 4, 1961, 887 - 890

TEXT: The authors tried (1) to check the data by R. Schuler et al. (Ref. 5. see below) on the protective action of the phenyl ring in radiolysis; (2) to obtain additional data on this protective action. The yields of primary radicals in the y-radiolysis of toluene, ethyl benzene, cumene, n-butyl benzene, n-octyl benzene, equimolecular mixtures of octane and benzene, and (for comparison) the radical yields of benzene, n-hexane, and n-octane were measured. The spectrophotometrically measured iodine concentration was 5.10⁻⁴ - 5.10⁻³ M. It did not affect the radical yield. By repeatedly

freezing up the substances in the vacuum, air was removed. Co⁶⁰ served as irradiation source. The dose measured by an FeSO₄ dosimeter was 1.3.10¹⁸ ev/literesec. The data are given in Table 1 and compared with R. Schuler's.

ev/liter sec. The data are given in Table 1 and compared with R. Schuler's Card 1/3'

32305 S/020/61/141/004/011/019 B101/B110

Intramolecular transfer of energy

The additive yield was calculated from the equation $G_{add} = \epsilon_A G_A + \epsilon_{Ph} G_{Ph}$ Here, \mathcal{E}_{A} , \mathcal{E}_{Ph} are the electronic fractions of the aliphatic chain and the aromatic ring, respectively; G_{A} , G_{Ph} are the radical yields of alkanes and benzene, respectively. The remarkably low yield for toluene was checked several times by means of samples purified by various methods. values found deviated only slightly from the data given in Table 1. Comparison of the data for octyl benzene and octane + benzene (1:1) permits the conclusion that the intramolecular transfer of energy in octyl benzene is more effective than the intramolecular energy transfer from the aliphatic chain of a molecule to the phenyl ring of another molecule. For the radical yield, the following is derived: $\begin{array}{l} G_{add} = G = \mathcal{E}_{A} \left[\Theta / (1 + \Theta) \right] \left(G_{A} - a_{A} G_{Ph} / a_{Ph} \right) \text{ (4), where} \\ O = \left(k_{M} + k_{APh} \left[Ph \right] \right) / \left(k_{\tilde{A}} + k_{A} \right) \text{ (5)} \quad k_{\tilde{A}} \text{ and } k_{Ph} \text{ are the constants of the} \end{array}$ rate of formation of radicals from the corresponding excited molecules or groups; k is the deactivation constant; k APh the constant of velocity of intermolecular energy transfer from the aliphatic chain to the phenyl ring; Card 2/54

32305 \$/020/61/141/004/011/019 B101/B110

Intramolecular transfer of energy ...

 $\lceil \mathtt{Ph} \rceil$ is the concentration of the phenyl rings; $k_{\mathtt{M}}$ the constant of velocity of intramolecular energy transfer from the aliphatic chain to the phenyl ring; aA, aPh are the factors of proportionality, i. e., the yields of excited molecules per unit of absorbed energy. G add - G was found to be a linear function of $\epsilon_{_{\mbox{\scriptsize A}}}$. The straight line passes through the origin of coordinates. Therefrom, it follows that $\theta/(1+\theta)$ is approximately constant. An evaluation of the ratio $a_A/a_{\rm ph}$ confirms that the intramolecular transfer of energy in octyl benzene takes place more probably than the intermolecular energy transfer from aliphatic chains to phenyl rings. The statements by P. Avivi, A. Weinreb (see below) saying that the energy transfer from polystyrene to 2,5-diphenyl oxazol or anthracene does not depend on whether the luminophore molecule is chemically bound to the polystyrene molecule do not contradict the above-mentioned opinion. The energy absorbed by the aliphatic chain is transferred to the neighboring phenyl ring of polystyrene. Luminescence arises due to the intermolecular energy transfer from the phenyl ring to the luminophore. There are 1 figure, 1 table, and 8 references: 1 Soviet and 7 non-Soviet. Card 3/34

S/020/61/141/004/011/019
Intramolecular transfer of energy... S/020/61/141/004/011/019

The four most recent references to English-language publications read as follows: Ref. 5: E. Weber, P. Forsyth, R. Schuler, Radiation Res., 3, 68 (1955); R. Schuler, J. Phys. Chem., 63, 925 (1959); A. Schapiro, J. Phys. Chem., 63, 801 (1959); P. Avivi, A. Weinreb, J. Chem. Phys., 27, 716 (1957).

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova (Physico-chemical Institute imeni L. Ya. Karpov)

PRESENTED: July 6, 1961, by S. S. Medvedev, Academician

SUBMITTED: May 22, 1961

Legend to Table 1: (1) substance; (2) data by Schuler; (3) data by the authors; $G_{a\mu} = G_{add}$; (a) benzene; (b) toluene; (c) ethyl benzene; (d) cumene; (e) butyl benzene; (f) octyl benzene; (g) octane + benzene (1:1); (h) hexane; (i) octane; (k) note: mean values of G are given.

Card 4/\$ 4

5/844/62/000/000/007/129 D290/D307

AUTHOR:

Bagdasar'yan, Kh. S.

Taran:

Deviations from additivity in radiation chemistry and their connection with energy transfer mechanisms

SOURCE:

Trudy II Vsesoyuznogo soveshchaniya po radiatsionnoy khimii. Ed. by L. S. Polak. Moscow, Izd-vo AN SSSR, 1962,

The author reviews the experimental results concerning the deviations from radiation-chemical additivity that occur in liquid phase systems containing organic components, and discusses the enerby transfer mechanisms that cause these deviations. The systems are divided into those showing small deviations from additivity and those showing large deviations; this division reflects the different mechanisms that cause the deviations in the two classes. In certain cases it is necessary to consider intramolecular energy transfer as well as the various processes of intermolecular energy transfer. There are 3 figures and 1 table.

Card 1/2

"APPROVED FOR RELEASE: 06/06/2000 CIA-RDP86-00513R000103010011-4

Deviations from additivity ... \$/844/62/000/000/007/129 D290/D507

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova (Physico-Chemical Institute im. L. Ia. Karpov)

Card 2/2

S/844/62/000/000/009/129 D290/D307

AUTHORS: Bagdasar'yan, Kh. S., Izrailevich, N. S. and Krongauz,

TITLE: Intramolecular migration of energy in irradiated alkylbenzenes

SOURCE: Trudy II Vsesoyuznogo soveshchaniya po radiatsionnoy khimii. Ed. by L. S. Polak. Moscow, Izd-vo AN SSSR, 1962, 70-73

TEXT: The authors measured the radical yields after the irradiation of toluene, ethylbenzene, cumene, n-butylbenzene, n-octylbenzene, benzene, n-hexane, n-octane, and an equimolecular mixture of benzene and n-octane with Co rays; iodine was used as a radical acceptor. In general, the radical yields were lower for the alkylbenzenes than would be expected if the yields were additive; in particular, the radical yield was much lower for octylbenzene than for the octane-benzene mixture. From these results the probabilities of intra- and intermolecular energy transfers are cal-

"APPROVED FOR RELEASE: 06/06/2000 CIA-RDP86-00513R000103010011-4

Intramolecular migration of ...

S/844/62/000/000/009/129 D290/D307

culated, concluding that intramolecular energy transfers from the aliphatic chain to the phenyl ring are much more probable than intermolecular energy transfers between separate aliphatic chains and phenyl rings. There is all figure and 1 table.

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova (Physico-Chemical Institute im. L. Ya. Karpov)

Card 2/2

11. 1265 5. 4600

37517 \$/020/62/144/001/014/024 B119/B144

AUTHORS:

Bagdasar'yan, Kh. S., Krongauz, V. A., and Kardash, N. S.

TITLE:

The mechanism of protective action of aromatic amines in the radiolysis of polymers. The sensitized formation of ion

radicals of amines

PERIODICAL: Akademiya nauk SSSR. Doklady, v. 144, no. 1, 1962, 101 - 104

TEXT: The protective action of p-naphthyl amine, phenyl-p-naphthyl amine, diphenyl amine, and triphenyl amine against destruction of polymethyl methacrylate (molecular weight ~7·10⁶ and ~10⁶) caused by y-radiation was studied. Co⁶⁰ was used as radiation source (6.6·10¹⁸ ev/liter·sec). Polymer films 100 thick with different contents of protective agent (up to 0.2 moles/liter) were subjected to y-radiation in vacuo at room temperature and -196°C. The number G of chain ruptures was determined on the basis of the mean molecular weight of the polymer after irradiation. The content of protective agent before and after irradiation was determined spectrophotometrically after dissolution and coupling with p-nitro-benzoyl

Card 1/3

S/020/62/144/001/014/024 B119/B144

The mechanism of protective action ...

diazonium. The spectra of the films irradiated at -196°C were taken at the same temperature by means of a special quartz Dewar vessel as cuvette. Results: At room temperature, the number C of chain ruptures is, in all cases, independent of the radiation dose; it depends on the amount of protective agent in the film. G is 1.7 with pure polymer; phenyl-s-naphthyl amine in amounts of 0.2 moles/liter reduces C to 0.65. Similar results were obtained with the other amines. At -196°C, G depends to a limiting value on the radiation dose. At this temperature, G = 0.8 for pure polymer, and 0.4 with 0.05 moles/liter of triphenyl amine. At low radiation doses, the consumption of phenyl-p-naphthyl amine is 1-2 molecules per 100 ev energy. On irradiation at -1960C, the films are pink, green, or blue according to the amine content. The coloring is due to the formation of ion radicals in the amines which are not immediately neutralized by electrons at this temperature. The ion radicals are formed by transfer of the energy absorbed by the substrate (polymer, in this case) to the amine. The protective action of aromatic amines is explained by these energy transfers. There are 4 figures. The most important English-language references are: L. Wall, D. Brown, J. phys. Chem., 61, 129 (1957); G. Lewis, D. Lipkin, J. Am. Chem. Soc., 64, 2801 (1942).

Card 2/3

CIA-RDP86-00513R000103010011-4 "APPROVED FOR RELEASE: 06/06/2000

The mechanism of protective action...

S/020/62/144/001/014/024 B119/B144

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova (Physico-

chemical Institute imeni L. Ya. Karpov)

PRESENTED: November, 17, 1961, by S. S. Medvedev, Academician

SUBMITTED: November 1, 1961

Card 3/3

1:451:4

S/020/62/147/006/029/034 B144/B186

15 7350

AUTHORS:

Bagdasar'yan, Kh. S., Sinitsyna, Z. A.

TITLE:

Sensibilized formation of ion-radicals of aromatic amines in the radiolysis of frozen organic glasses

PERIODICAL: Akademiya nauk SSSR. Doklady, v. 147, no. 6, 1962, 1396-1398

TEXT: Continuing earlier studies (DAN, 144, 101 (1962)), the formation of cation-radicals was studied in organic glass frozen at -196°C and gamma-irradiated with 4.1°10¹⁵ ev/g*sec. This glass contained 0.005 mole/l diphenyl or triphenyl amine dissolved in isopentane and methyl cyclohexane. The glass became blue-green (absorption maximum at 670 mm) and the optical density increased proportionally to the dose up to 7.10¹⁸ ev/g and then remained then constant. With a dose of 7.3°10¹⁸ ev/g, the ion-radical concentration reached a constant value at an amine concentration of 0.005 mole/l. The value of this critical concentration was derived from tests with triphenyl amine. Taking the same value for the absorption coefficient of the triphenyl amine cation-radical as for tri-

Card 1/3 11 NOT SELECTED FOR ABSTRACTUS

Sensibilized formation of ...

S/020/62/147/006/029/034 B144/B186

tolyl amine, namely 1.1.104; and using the optical density as found to be 0.080, the result was $C = 0.080/1.1 \cdot 10^4 \cdot 0.5 = 1.5 \cdot 10^{-5}$ mole/1. This value is by two orders less than that for triphenyl in polymethyl methacrylate, owing to the electron-acceptor activity of the ester group. The radiation yield of the cation-radicals is 0.16 in relation to the total energy absorbed by the amine. This value, which is 10 times higher than the energetically possible values, confirms the earlier conclusion that the cation-radical formation is not due to a direct radiation effect on the amines. Addition of CCl4 increased the cation-radical yield from irradiated diphenyl amine; the critical concentration was 0.05 mole/1 CClA. It is still not clear why CCl4 had no effect on triphenyl amine. Even in 1:3 mixtures of diphenyl and triphenyl amines, only diphenyl cation-radicals was formed; the optical density at 670 mm was slightly reduced, but the value 640 mm, which is characteristic of triphenyl amine showed no increase. This unequal behavior of the two amines confirms the absence of a direct radiation effect on the amines. Tre energy transfer is directed toward the diphenyl amine which is the stronger electron-donor. Card 2/3

Sensibilized formation of ...

S/020/62/147/006/029/034 B144/B186

0.005 mole/1 additions of anisole, tetrahydrofuran and naphthalene proved ineffective. There are 4 figures.

ASSOCIATION: Fiziko-khimicheskiy institute im. L. Ya. Karpova (Physicochemical Institute imeni L. Ya. Karpov)

PRESENTED:

July 19, 1962, by N. M. Zhavoronkov, Academician

SUBMITTED:

July 14, 1962

Card 3/3

CHICHIBABIN, Aleksey Yevgen'yevich. Prinimali uchastiye: REUTOV,
O.A.; KITAYGORODSKIY, A.I., prof.; LIBERMAN, A.L., doktor
khim. nauk; BAGDASAR'YAN, Kh.S., doktor khim. nauk; PLATE,
N.A., kand. khim. nauk; KOLOSOV, M.N., kand. khim. nauk;
BOTVINIK, M.M., doktor khim. nauk; STEPANOV, V.M., kand.
khim. nauk; MEL'NIKOV, N.N., prof.; DEREVITSKAYA, V.A.,
doktor khim. nauk; LIBERMAN, A.L., red.; SERGEYEV, P.G.
[deceased]; ROMM, R.S., red.; SHPAK, Ye.G., tekhn. red.

[Basic principles of organic chemistry] Osnovnye nachala organicheskoi khimii. Izd.7. Pod red. P.G.Sergeeva i A.L. Libermana. Moskva, Goskhimizdat. Vol.1. 1963. 910 p. (MIRA 16:10)

1. Chlen-korrespondent AN SSSR (for Reutov). (Chemistry, Organic)

BAGDASAR'YAN, Kh.S.; NEPOMNYASHCHIY, A.I.

Determination of absolute rates of chain growth and initiation in amionic polymerization of styrene. Kin.i kat. 4-no.1:60-66 Ja-F '63. (MIRA 16:3)

· 1822 -

1. Fiziko-khimicheskiy institut imeni L.Ya.Karpova.
(Styrene polymers) (Chemical reaction, Rate of)

BAGDASAR'YAN, Kh. S.; SINITSYNA, Z. A.

Sensibilized formation of ion radicals of aromatic amines in the radiolysis of frozen organic glasses. Dokl. AN SSSR 147 no.6:1396-1398 D 162. (MIRA 16:1)

1. Fiziko-khimicheskiy institut im. L. Ya. Karpova. Predstavleno akademikom N. M. Zhavoronkovym.

(Amines) (Resins, Synthetic) (Gamma rays)

NEPOMNYASHCHIY, A.I.; BAGDASAR'YAN, Kh.S.

Effect of the nature of an alkali metal and of the solvent on the absolute rate constants in anionic polymerization of styrene. Kin.i kat. 4 no.2:198-203 Mr-Ap *63. (MIRA 16:5)

1. Fiziko-khimicheskiy institut imeni L.Ya.Karpova.
(Styrene) (Polymerization) (Alkali metals)

L 10703-63 EMP(j)/EPF(c)/FMT(1)/EWT(m)/BDS-AFFTC/ASD-Pc-1/Pr-1-RM/HM ACCESSION NR: AP3002023 S/0195/63/004/003/0489/0491

AUTHOR: Pshiby*lovich, Z. V.; Krongauz, V. A.; Bagdasar'yan, Kh. S.

TITLE: Study of the radiolysis of some hydrocarbons by gas chromatography and electron paramagnetic resonance.

SOURCE: Kinetika i kataliz, v. 4, no. 3, 1963, 489-491

TOPIC TAGS: radiolysis, hydrocarbons, gas chromatography, electron paramagnetic resonance, alkyl benzenes, intramolecular energy migration, Gamma rays, n-octane, n-octylbenzene

ABSTRACT: The purpose of this work was to verify earlier conclusions that alkylbenzenes are appreciably more stable to irradiation than expected when independent radiolytic decomposition of side chain and ring is postulated. Analyses of data obtained showed that intramoleculear energy migration is at least five times more probable than intermolecular transfer. The main gaseous product of irradiation of n-octane, an equimolecular mixture of octane and benzene and n-octylbenzene with Gamma-rays from Co sup 60 was hydrogen in yield independent of dose up to 100 megarad and falling in the sequence shown. The low hydrogen yield from n-octylbenzene is ascribed to intermolecular migration of energy from side chain to

Card 1/2

"APPROVED FOR RELEASE: 06/06/2000 CIA-RDP86-00513R000103010011-4

L 10703-63

ACCESSION NR: AP3002023

benzene ring. From EPR spectra it is suggested the radical formed from n-octylbenzene has the unpaired electron on the carbon adjacent to the benzene nucleus and that this is the site of the bond breakage. Orig. art. has:2 figures and 1

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova (Physicochemical Institute)

SUBMITTED: 10Jul62

DATE ACQ: 12Jul63

ENCL: 00

SUH CODE: 00

NO REF SOV: 004

OTHER: 006

Card 2/2